Docket No. 243042US0

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF: Geoffrey A. SCARSBROOK, et al. GAU: 1771

SERIAL NO: 10/665,550

FILED: September 22, 2003

FOR: SINGLE CRYSTAL DIAMOND

REQUEST FOR PRIORITY

COMMISSIONER FOR PATENTS
ALEXANDRIA, VIRGINIA 22313

SIR:

☐ Full benefit of the filing date of U.S. Application Serial Number , filed , is claimed pursuant to the provisions of **35 U.S.C. §120**.

☐ Full benefit of the filing date(s) of U.S. Provisional Application(s) is claimed pursuant to the provisions of **35 U.S.C. §119(e)**: **Application No.** **Date Filed**

■ Applicants claim any right to priority from any earlier filed applications to which they may be entitled pursuant to the provisions of **35 U.S.C. §119**, as noted below.

In the matter of the above-identified application for patent, notice is hereby given that the applicants claim as priority:

COUNTRY	APPLICATION NUMBER	MONTH/DAY/YEAR
Great Britain	GB 0221949.1	September 20, 2002

Certified copies of the corresponding Convention Application(s)

- ■ are submitted herewith
- ☐ will be submitted prior to payment of the Final Fee
- ☐ were filed in prior application Serial No. filed
- ☐ were submitted to the International Bureau in PCT Application Number
  Receipt of the certified copies by the International Bureau in a timely manner under PCT Rule 17.1(a) has been acknowledged as evidenced by the attached PCT/IB/304.
- ☐ (A) Application Serial No.(s) were filed in prior application Serial No. filed ; and
- ☐ (B) Application Serial No.(s)
  - ☐ are submitted herewith
  - ☐ will be submitted prior to payment of the Final Fee

Respectfully Submitted,

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I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

I also certify that the application is now proceeding in the name as identified herein.

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Signed Stephen Hordley.

Dated 20 October 2003

GB0221949.1

By virtue of a direction under Section 32 of the patents Act 1977, the application is proceeding in the name of,

ELEMENT SIX LIMITED,
Incorporated in the United Kingdom,
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IM99 6AQ,
United Kingdom

[ADP No. 08479958001]

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1/77

22SEP02 E750019-3 D00019
P01/7700 0.00-0221949.1

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1.	Your reference	**PA133351/P (P031872GB)**
2.	Patent application number *(The Patent Office will fill in this part)*	0221949.1 20 SEP 2002
3.	Full name, address and postcode of the or of each applicant *(underline all surnames)*	**Diamanx Products Limited** **Isle of Man Freeport** **Ballasalla** **Isle of Man** **IM99 6AQ** SECTION 32 (1977 ACT) APPLICATION FILED 31/03/03
	Patents ADP number *(if you know it)*	7153772002
	If the applicant is a corporate body, give the country/state of its incorporation	**Isle of Man, U.K.**
4.	Title of the invention	**Single Crystal Diamond**
5.	Name of your agent *(if you have one)*	**Carpmaels & Ransford**
	"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*	**43 Bloomsbury Square** **London** **WC1A 2RA**
	Patents ADP number *(if you know it)*	**83001**

6.	If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number	Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7.	If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application	Date of filing *(day / month / year)*

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a) any applicant named in part 3 is not an inventor, or
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Description	12
Claim*(s)*	
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Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
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Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature Carpmaels & Ransford — Date

Carpmaels & Ransford — **20th September 2002**

12. Name and daytime telephone number of person to contact in the United Kingdom — **Mr. A.J. Jones** — **020-7242 8692**

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BACKGROUND OF THE INVENTION

This invention relates to single crystal diamond.

Diamond offers a range of unique properties, including optical transmission, thermal conductivity, stiffness, wear resistance and its electronic properties. Whilst many of the mechanical properties of diamond can be realised in more than one type of diamond, other properties are very sensitive to the type of diamond used. For example, for the best electronic properties CVD single crystal diamond is important, often outperforming polycrystalline CVD diamond, HPHT diamond and natural diamond.

In many applications of diamond the limited lateral dimensions of the diamond available are a substantial limitation. Polycrystalline CVD diamond layers have substantially removed this problem for applications where the polycrystalline structure is suitable for the application, but in many applications polycrystalline diamond is unsuitable.

Whilst natural and HPHT diamond may not be suitable for some applications, they are used as substrates on which to grow CVD diamond. Although substrates can have a variety of crystallographic orientation, the largest and most suitable substrate orientation which can be produced for growth of high quality CVD diamond is generally (001). Throughout this specification, the Miller indices {hkl} based on the axes x,y,z will be written assuming the z direction is that normal to the substrate surface and parallel to the growth direction. The axes x,y are then within the plane of the substrate, and are

generally equivalent by symmetry but distinct from z because of the growth direction.

Large natural single crystal diamond is extremely rare and expensive, and large natural diamond substrate plates suitable for CVD diamond growth have not been demonstrated because of the associated very high economic risk in their fabrication and use. Natural diamond is often strained and defective, particularly so in larger substrate plates, and this causes twins and other problems in the CVD overgrowth or fracture during synthesis. In addition, dislocations which are prevalent in the natural diamond substrate are replicated in the CVD layer, also degrading its electronic properties.

HPHT synthetic diamond is also limited in size, and generally is of poorer quality in the larger stones, with inclusions being a major problem. Larger plates fabricated from synthetic diamonds generally exhibit missing corners so that edge facets other than {100} (such as {110}) are present, or they are included or strained. During synthesis further facets are formed, such as the {111} which lies between the (001) top face and the {110} side facets (see Figure 1 of the accompanying drawings). In recent years significant effort has been directed at synthesising HPHT diamond of high quality for applications such as monochromators, and some progress has been reported, but the size of HPHT plates suitable for substrates remains limited.

{111} faces in particular are known generally to form twins during CVD synthesis of thick layers, limiting the area of perfect single crystal growth and often leading to degradation and even fracture during synthesis, further exacerbated by thermal stresses resulting from the growth temperature. Twinning on the {111} particularly interferes with increasing the size of the largest plate with a (001) major face which can be fabricated to be bounded only by {100} side faces.

Routinely available (001) substrates suitable for high crystal quality CVD synthesis range up to about 7 mm square when bounded by {100} edges, and up to about 8.5 mm across the major face when bounded by {100} and {110} edges, although the largest area inscribed rectangular plate bounded by {100} edges generally remains about 7 mm square.

CVD homoepitaxial synthesis of diamond involves growing CVD epitaxially on an existing diamond plate and is well described in the literature. This is of course still limited by the availability of existing diamond plates. In order to achieve larger areas, the focus has been to grow laterally as well, increasing the overall area of the overgrown plate. Such a method is described in EP 0 879 904.

An alternative to homoepitaxial growth is heteroepitaxial growth, where a non-diamond substrate is grown on with an epitaxial relationship. In all reported cases however, the product of this process is quite distinct from homoepitaxial growth, with low angle boundaries between highly oriented but not exactly oriented domains. These boundaries severely degrade the properties of the diamond.

Another alternative proposed to increase the area of a single crystal diamond plate is the method of tiling. In tiling an array of plates are carefully fabricated and placed in a close fitting array with the crystallographic orientation of the material aligned. However, as with heteroepitaxial growth, the alignment between adjacent plates is not perfect, and low angle boundaries in the material grown above substrate boundaries are inevitable. Furthermore, imperfections in the assembly of the array of plates usually introduces additional dislocations or other defects at the boundaries.

The boundaries formed in the methods of tiling and heteroepitaxial growth directly degrade the electronic properties of the material in which they are

formed, but in addition are replicated in any growth on top of the layer incorporating these boundaries, and in the particular case of growing high purity material form visible macroscopic surface features which cause further crystal degradation.

Homoepitaxial diamond growth to enlarge the area of a CVD plate presents many difficulties.

If it was possible to achieve ideal homoepitaxial growth on a diamond plate, the growth which would be achieved is substantially that illustrated by Figures 1 and 2 of the accompanying drawings. The growth morphology illustrated assumes that there is no competing polycrystalline diamond growth. However, in reality, there is generally competition from polycrystalline growth, growing up from the surface on which the diamond substrate plate is mounted. This is illustrated by Figure 3 of the accompanying drawings.

Referring to Figure 3, a diamond substrate plate 10 is provided mounted on a surface 12. Example materials for surface 12 include molybdenum, tungsten, silicon and silicon carbide. During CVD diamond growth, single crystal diamond growth will occur on the (001) face 14 and on the side surfaces, two of which 16 are shown. The side surfaces 16 are {010} surfaces. Growth will also occur on and extend outwards from the corners 18 of the plate. All such growth will be homoepitaxial single crystal growth. The growth on each of the faces present on the substrate, and on any new surfaces generated during growth, constitutes a growth sector. For example, in Figure 3 diamond growth 24 arises from the {101} plane and thus is the {101} growth sector.

Competing with the homoepitaxial single crystal growth will be polycrystalline diamond growth 20 which will take place on the surface 12. Depending on the thickness of the single crystal diamond layer produced on the surface 14, the

polycrystalline diamond growth 20 may well meet the homoepitaxial single crystal diamond growth along line 22, as illustrated in Figure 3.

Based on Figure 2, one might expect that the purely lateral growth on the substrate sides could be used to fabricate a larger substrate, including the material of the original substrate. However, as is clear from Figure 3, such a plate would actually contain competing polycrystalline growth. A plate fabricated parallel to the original substrate, but higher up in the grown layer is likely to contain twinning, especially from material in the {111} growth sector.

Under growth conditions where polycrystalline diamond does not compete with the single crystal diamond there still remains the problem that the quality of the lateral single crystal growth is generally poor, as a result of the different geometry and process conditions present at the diamond substrate edges, exacerbated by the method used to suppress polycrystalline growth.

SUMMARY OF THE INVENTION

According to the present invention, a method of producing a plate of single crystal diamond includes the steps of providing a diamond substrate having a surface substantially free of surface defects, growing diamond homoepitaxially on the surface by chemical vapour deposition and severing the homoepitaxial CVD grown diamond and the substrate with one or more cuts non-parallel to the substrate surface on which growth took place, the cuts being typically normal (that is, at or close to an angle of 90°) to the surface of the substrate on which diamond growth took place, to produce a plate of single crystal diamond.

The homoepitaxial CVD diamond growth on the surface of the substrate preferably takes place by the method described in WO 01/96634. Using this method, in particular, it is possible to grow thick, high purity single crystal

diamond on a substrate. Growth thicknesses of greater than 10mm, preferably greater than 12mm, and more preferably greater than 15mm, can be achieved. Thus, it is possible, by the method of the invention, to produce single crystal diamond plates having an axis or largest lateral dimension exceeding 10mm. In particular, it is possible by the method of the invention, to produce rectangular (001) single crystal diamond plates which are bounded by {100} sides which have a largest lateral edge dimension exceeding 10 mm.

The plate of single crystal diamond produced by the method may then itself be used as a substrate in the method of the invention. Thick single crystal diamond can be grown homoepitaxially on a major surface of the plate.

The invention provides, according to another aspect, a single crystal diamond plate having major surfaces on opposite sides thereof, each major surface having an axis or largest lateral dimension exceeding 10mm. In one form of the invention, the plate has a rectangular, square, parallelogram or like shape, with at least one lateral dimension or pair of sides, and preferably two lateral dimensions or pairs of sides, which exceed 10mm. In particular, it is possible by the method of the invention, to produce rectangular (001) single crystal diamond plates which are bounded by {100} sides which have both lateral edge dimensions exceeding 10 mm.

In the homoepitaxial diamond growth which occurs on the surface of the diamond substrate, any dislocations or defects in that surface, or arising at the interface with the substrate, or from the edges of the substrate, generally propagate vertically in the diamond growth. Thus, if the severing takes place substantially perpendicular to the surface on which diamond growth took place, then the severed surface will have substantially no dislocations within the material intersecting the surface, as they will be running generally parallel to the surface. Thus a reduction in the dislocation density in the volume of the material can be achieved by repeating the method using this new plate as the

substrate, and a resulting further reduction in the density of dislocations cutting the major surface of any plates cut normal to this substrate.

Generally the highest quality CVD growth is that contained within the vertical (001) growth sector. Furthermore, since the edges of the substrate can form dislocations and these generally rise vertically upwards, then the highest quality volume of the CVD growth is that bounded by the vertical planes rising up from the substrate edges. The method of this invention enables one or more new large area plates to be fabricated from entirely within this volume, thus minimising the defects within the plate, and maximising its crystal quality.

Combining the various features of this invention, it is possible to produce diamond with a lower dislocation density than the starting substrate material, with the lower limit on dislocation density set only by the number of times the method is to be repeated. In particular, the large area plate of the invention and any layers subsequently synthesised on it can have a dislocation density intersecting a surface normal to the growth direction (this surface generally showing the highest dislocation density in CVD diamond), which is less than $50/mm^2$, and preferably less than $20/mm^2$, and more preferably less than $10/mm^2$ and even more preferably less than $5/mm^2$. The defect density is most easily characterised by optical evaluation after using a plasma or chemical etch optimised to reveal the defects (referred to as a revealing plasma etch), using for example a brief plasma etch of the type described in WO 01/96634.

Where the substrate is a natural or HPHT synthetic substrate, it is generally not advantageous for the normally cut plate to include the material from the substrate, although this can be done. It may be advantageous to include material from the substrate in this plate when the substrate is itself a CVD diamond plate, which may itself have been prepared by this method.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic perspective view of a diamond plate on which ideal homoepitaxial diamond growth has taken place;

Figure 2 is a section along the line 2-2 of Figure 1;

Figure 3 is a section through a diamond plate illustrating single crystal diamond growth and polycrystalline diamond growth;

Figure 4 is a section through a diamond plate on which homoepitaxial diamond growth according to an embodiment of the invention has taken place.

DESCRIPTION OF AN EMBODIMENT

An embodiment of the invention will now be described with reference to Figure 4 of the accompanying drawings. Referring to Figure 4, a diamond plate 30 is provided. The diamond plate 30 is a plate of single crystal diamond. The upper face 32 is the (001) face and the side surfaces 34 are {010} faces. The surface 32 is substantially free of surface defects, more particularly substantially free of crystal defects generally achieved using the substrate preparation methods described in WO 01/96634.

Diamond growth 36 then takes place on the diamond substrate 30. This diamond growth occurs vertically on the upper surface 32, outwards from the corners 38 of the substrate 30 and outwards from the side surfaces 34. This diamond growth will generally be homoepitaxial, single crystal and of high crystal quality in the bulk of the volume, although dislocations and twinning on the {111} may be present as described earlier. The method of growth may follow that of WO 01/96634, although it is not limited to the method described therein. In particular, whilst the process is selected to produce material of high crystal quality in the bulk of the layer, it is not necessary that the process be of

high chemical purity, and elements such as B, N, S, P may be present in the gas phase of the synthesis process, and incorporated into the layers synthesised in low concentration. A large area plate produced by the method, which contains chemical impurities typically at a concentration of less than 10 ppm, and more typically at a concentration of less than 2 ppm, and even more typically at a concentration of less than 0.5 ppm, can be subsequently used as a substrate to synthesise a high purity plate without significant detriment.

Inevitably, some polycrystalline diamond growth will occur on the surface on which the substrate is placed. This polycrystalline diamond growth may, depending on the thickness of the diamond growth region 36, meet the lower surface 40 of this region.

Once a desired thickness of diamond growth 36 has taken place, the diamond growth region 36 and substrate 30 are severed normal (at approximately 90°) to the surface 32, as illustrated by dotted lines 44. This produces a plate 46 of high quality single crystal diamond. The interface between the original substrate and the diamond growth will, for practical purposes, be indistinguishable. The original substrate material may form part of plate 46 or be removed from it. More than one plate may be produced, with each plate parallel to the next and normal to the substrate.

Using the method of WO 01/96634, it is possible to produce a diamond growth region 36 which exceeds 10mm in depth. Thus, the diamond plate 46 which is produced will have sides 48 which exceed 10mm in length.

The plate 46 may be used as a substrate for the method of the invention. Thus, if the plate 46 has sides 48 greater than 10mm in length and diamond growth exceeding 10mm in thickness is produced on the surface 50 of the

plate, it is possible to produce a square, rectangular or similar shaped plate which has all four sides exceeding 10mm in length.

Severing in Figure 4 is shown to take place perpendicular to the surface 32. Severing can take place at angles other than perpendicular to the surface 32, excluding plates which are parallel to the substrate. Plates produced at angles other than normal to the substrate, where the substrate has a (001) major face, will have major faces other than the {100}, such as the {110}, {111}, {112}, {113}, or higher order planes.

Further, it is possible to sever along planes which are at right angles to the sever planes 44 of Figure 4, which will also form a plate with a major {100} face, or at any other angle relative to the sever planes 44, which will form plates with major faces of the type {hk0} referenced to the axes of the original (001) substrate. To achieve single crystal diamond plates, some trimming of polycrystalline or defective growth at the edges may be necessary.

Those skilled in the art will recognise that the general method need not be restricted to growth on substrates with a (001) major face, but could equally be applied to other substrates with, for example, {110}, {113}, or even {111} major faces, but that in general the preferred method is to use a substrate with a (001) major face, since the highest quality CVD diamond growth can be achieved on this face and the disposition of facets formed on the growing CVD on this face is generally most appropriate for the production of large plates cut from the material grown.

The key dimensions in a substrate plate with a (001) major face are those of the largest area rectangular plate which can be fabricated bounded only by {100} side faces. It has been determined that growth on this plate can relatively easily produce, using lateral growth, the plate bounded by {110} sides which is rotated by 45°, as shown in Figure 1, since this makes limited or no use of

{111} growth sector material. This new plate, bounded by {110} side faces has an area which is at least double that of the {100} bounded plate, but the original {100} bounded plate generally remains the largest inscribed {100} bounded plate which can be fabricated from it. Further growth on a plate partly or totally bounded by {110} edges immediately generates {111} facets and the associated problem of twinning, so that as a substrate plate this has no greater utility than the largest area inscribed {100} edged bounded plate that could be fabricated from it. Although methods of suppressing twinning using the 'alpha parameter' ($\alpha = \sqrt{3}\frac{V_{100}}{V_{111}}$, where V_{100} is the growth rate on the {100} and V_{111} is likewise for the {111}) have been proposed for many years, these have failed to demonstrate the fabrication of the large area plates of this invention. This parameter fails to take proper account of a number of parameters including, for example, the presence of facets other than the {100} and {111} (e.g the {110}).

For the above reasons, reference to the size of a single crystal diamond plate with a (001) major face in this specification often explicitly refers to the size of the largest area inscribed rectangular plate bounded by {100} edges, if the plate does not already have {100} edges.

In many final applications, the increased area of the substrate plate obtained by this simply obtainable rotation of the edge from {100} to {110} can be used beneficially. However it does not form a useful process to increasing indefinitely the area of the substrate plate.

Applications of the large area single crystal diamond plates of the invention include but are not limited to the following:

Electronic applications:- Since the plate of the invention is substantially free of dislocations and crystal defects over large areas, the plate is particularly suited to applications requiring high mobility, high lifetime, high electrical breakdown

voltage, or other high performance electronic properties. The plate can provide these properties over large single components where the application requires it, and also over large plates from which volume production can be achieved of smaller components with consistent properties.

Detector applications:- Diamond is well known as a potential detector material. The plate of this invention allows for large area single crystal diamond detectors which exhibit a uniform response to impinging particles or radiation over their entire area.

X-ray applications:- For single crystal diamond monochromators, the requirement is a uniform crystal structure with a very narrow peak in the X-ray rocking curve. The plate of this invention provides this, because of its low dislocation density.

Optical and other electromagnetic radiation applications:- Certain electromagnetic radiation applications are also sensitive to defect levels within diamond, as these can affect either the absorption, refractive index, or scattering locally. Specific examples include windows for high power beams, for example in the optical or microwave frequencies.

Further applications include large area optical windows for single or multi-spectral windows where diamond's other properties such as hardness, wear resistance, and thermal conductivity are also beneficial, and windows and other elements for watches, clocks, pendants, mobile phones, personal digital assistants (pdas), computers, and other domestic and commercial devices using display or optical communication technologies.

1/1

Fig 1

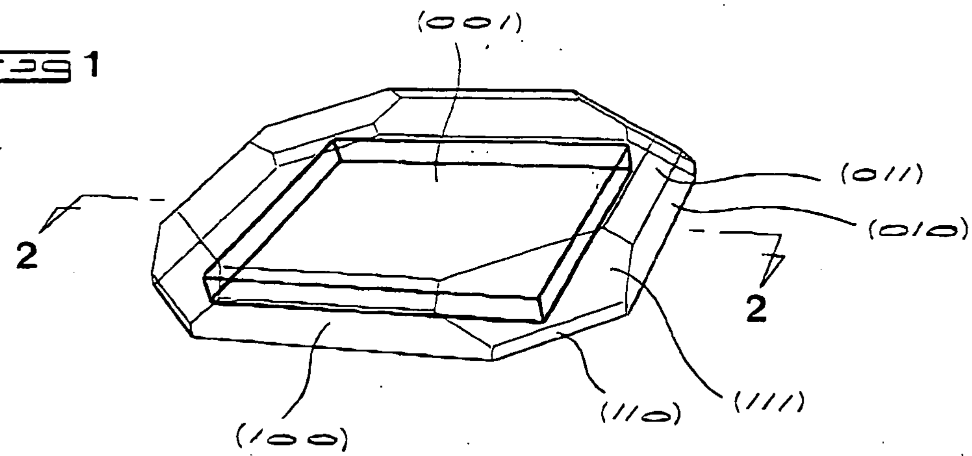


Fig 2

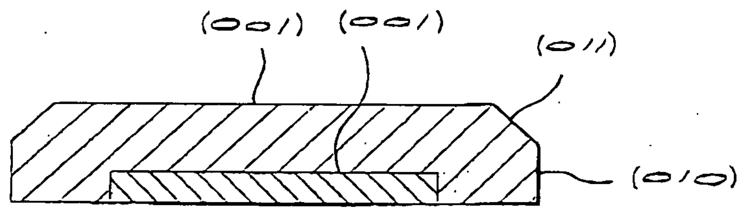


Fig 3

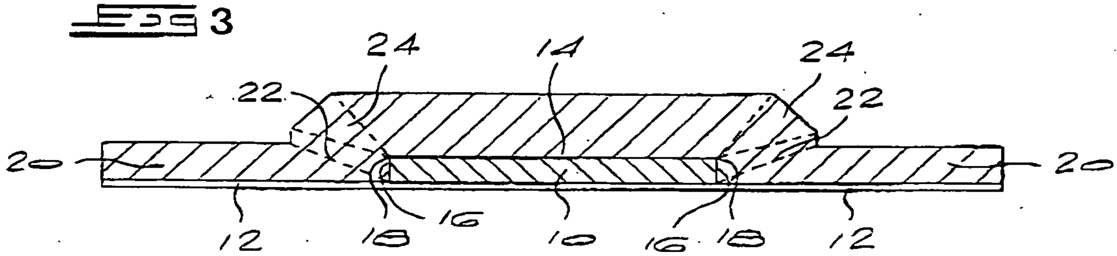
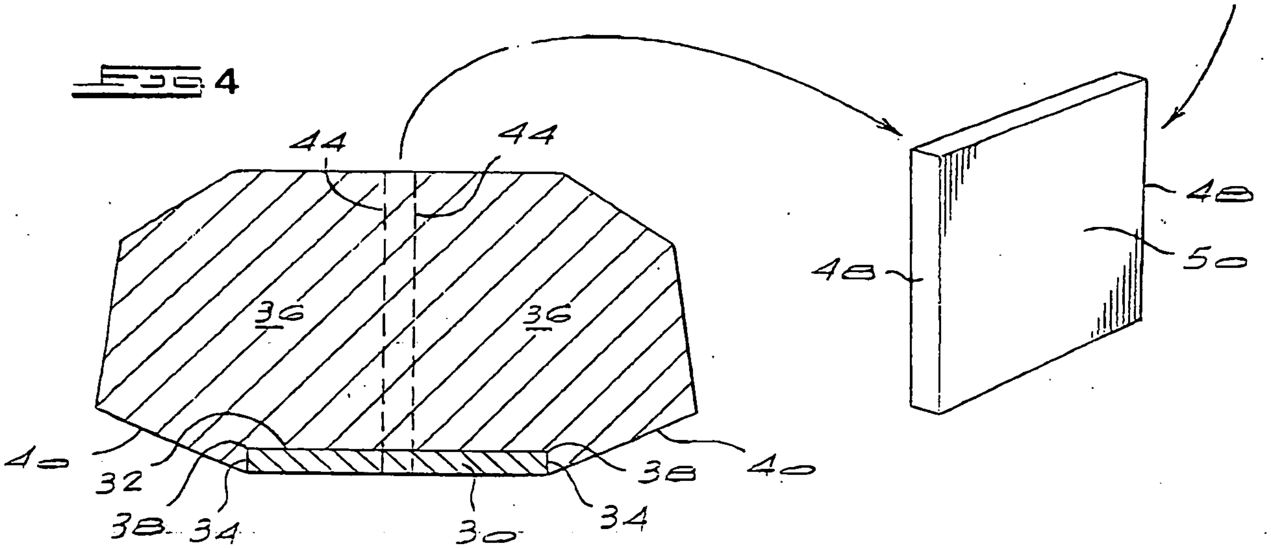


Fig 4



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